

**DOE/NSF Thermoelectric Partnership**  
**Project SEEBECK**  
**Saving Energy Effectively By Engaging in Collaborative**  
**research and sharing Knowledge**

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Report up to 16 March 2012

Project ID#: ACE068

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# Overview

## Timeline

Start: January 1, 2011  
End: December 31, 2014  
Percent complete: 31%

## Budget

Total (NSF+DOE): \$1,453,532  
DOE share: 50% (unverified)  
• Funding FY13:  
OSU+subcontracts: \$249,301  
NU: \$128,000  
VT: \$118,056

## Barriers

- Overall program barriers addressed: A, B, C, D
- Barriers specific to thermoelectric generators:
  - High-ZT low-cost materials made from available elements
  - Thermal management
  - Interface resistances
  - Durability
  - Metrology

## Partners

Ohio State University (OSU, lead), Northwestern University (NU), Virginia Polytechnic Institute and State University (VT), ZT Plus & BSST as subcontractors to OSU



# Objectives

**Project goal:** Develop elements for a practical automotive exhaust waste-heat recovery system that meets cost and durability requirements of the industry.

## Project objectives

1. Develop high-ZT low-cost materials made from available elements:
  - $ZT > 1.5$
  - materials that are not rare or toxic (Te, TI): **PbS, Mg<sub>2</sub>Sn, ZnSb**
2. New thermal management strategy, not developed under this program, in use at Gentherm
3. Minimize electrical and thermal interface resistances:
  - Compliant, to accommodate thermal expansion
  - High thermal conductance across interface
  - High electrical conductance across interface
4. Metrology:
  - Materials characterization
  - Electrical and Thermal interface resistance measurements
  - Overall system performance measurements
5. Durability:
  - Compatible with automotive durability requirements



# Objective 1: Materials

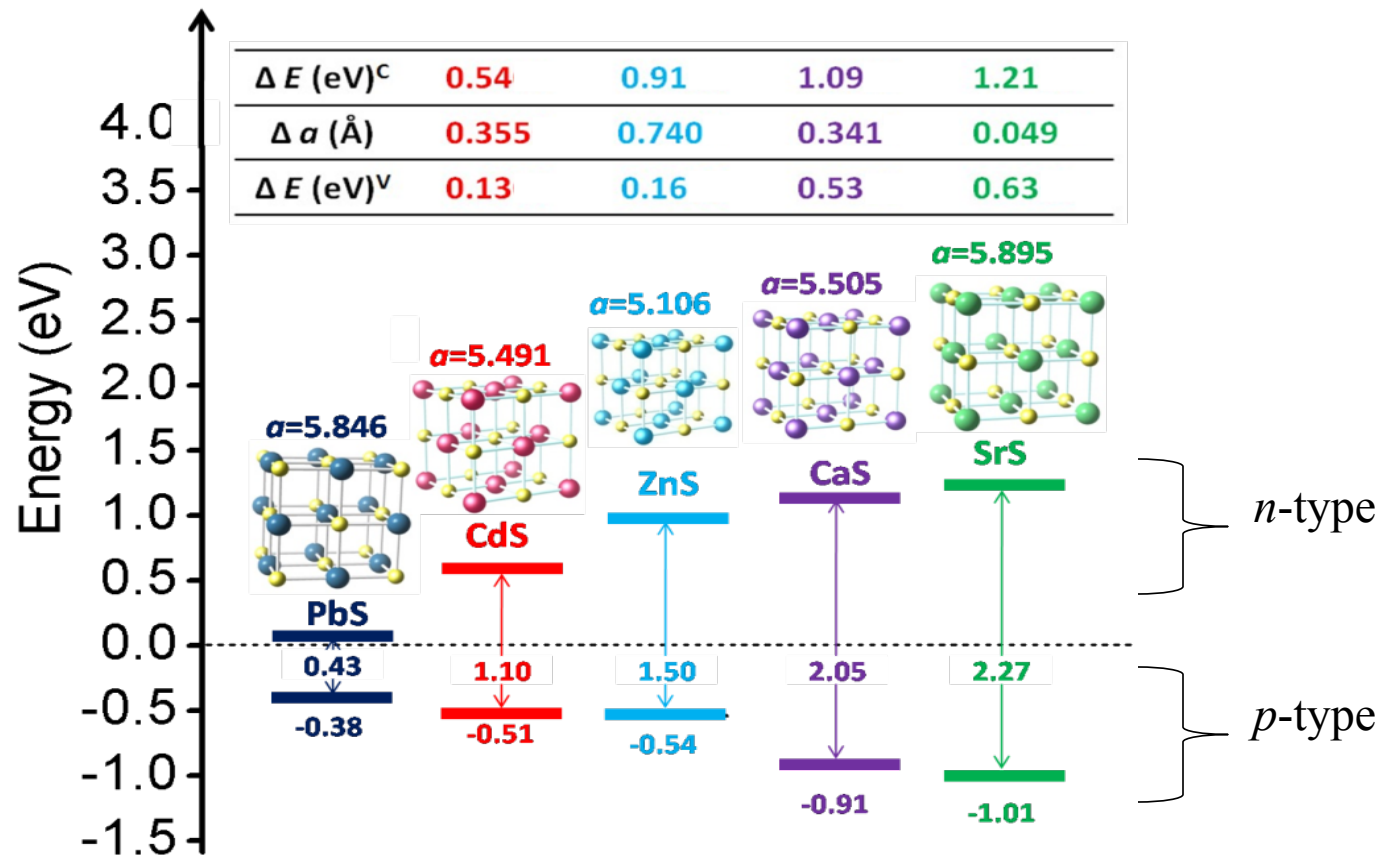
## Approach 1: PbS, the cheapest thermoelectric (Northwestern)

- PbS: the cheapest thermoelectric
- Raising  $ZT$  of p-type PbS with endotaxial nanostructuring and valence-band offset engineering using CdS and ZnS
- Band alignment engineering between nanostructures and matrix is a key path forward to increasing  $ZT$
- High performance in nanostructured p-type PbS ( **$ZT \sim 1.2-1.3$  at 900 K**):

**This is a breakthrough in the performance of PbS**

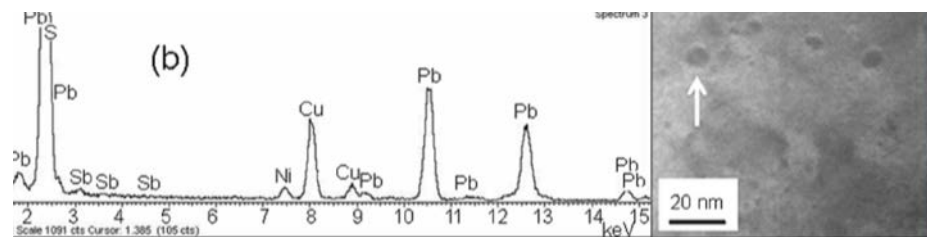
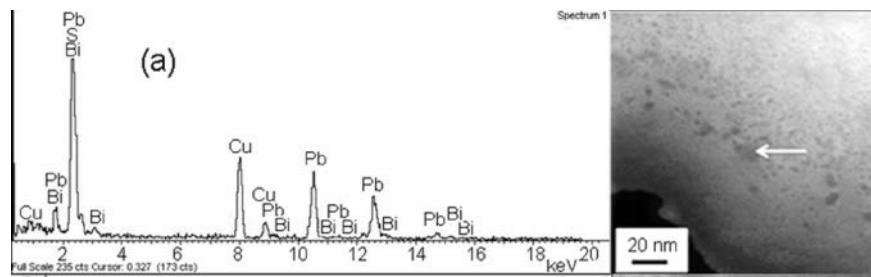
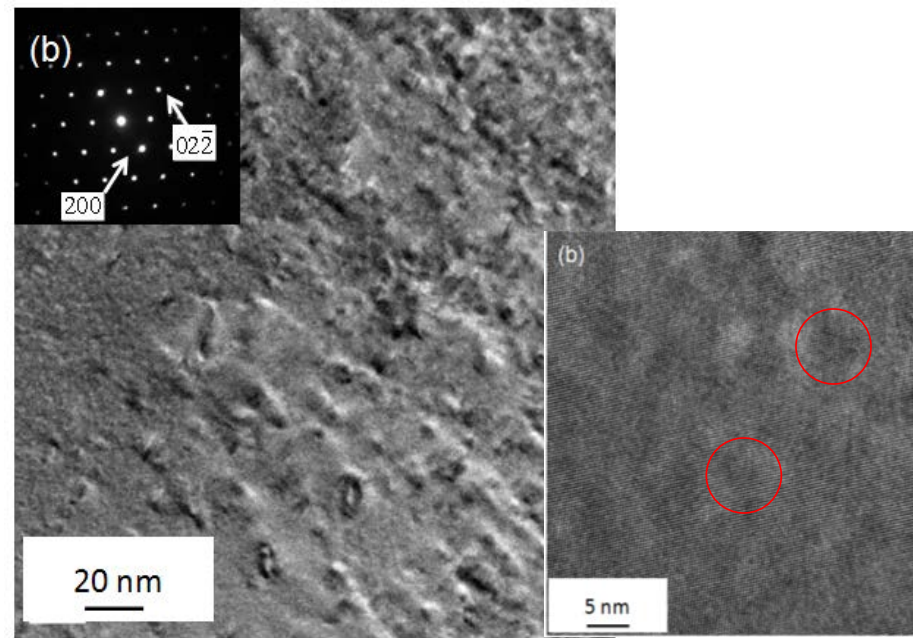
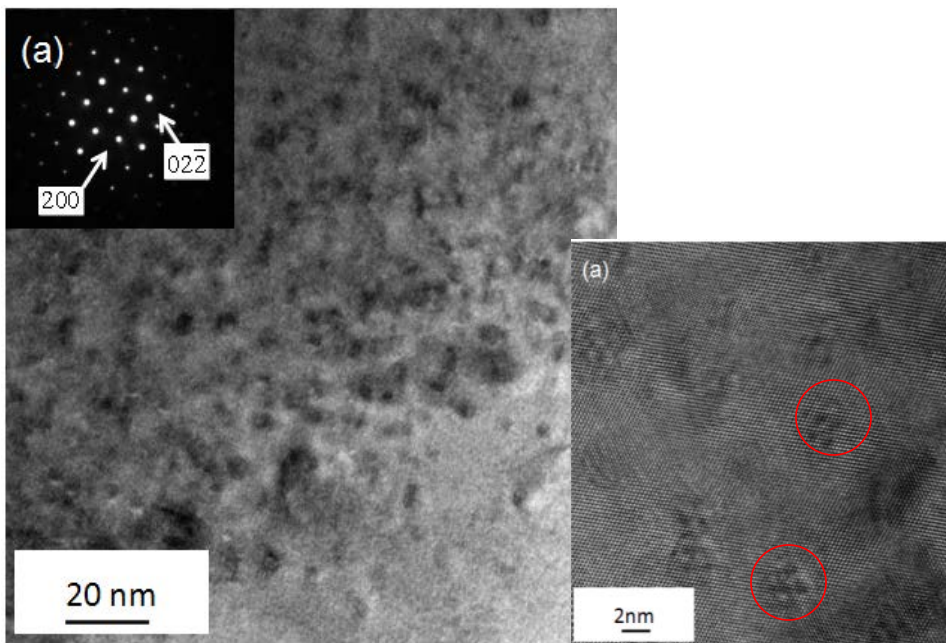
# PbS and MS second phases: band alignment

Band alignment engineering between nanostructures



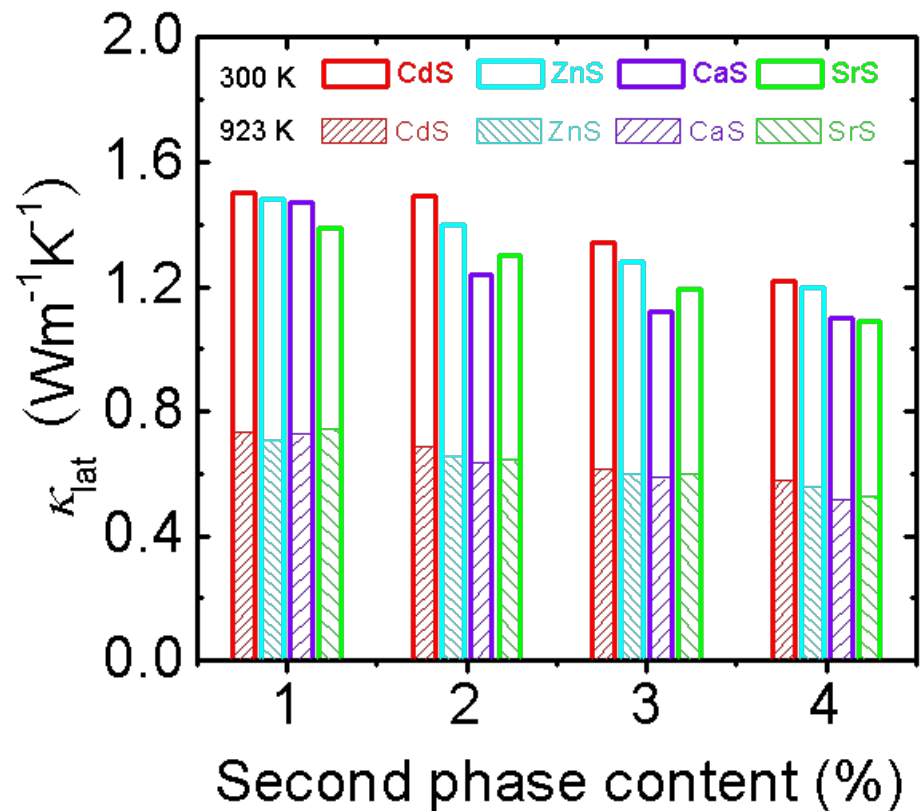
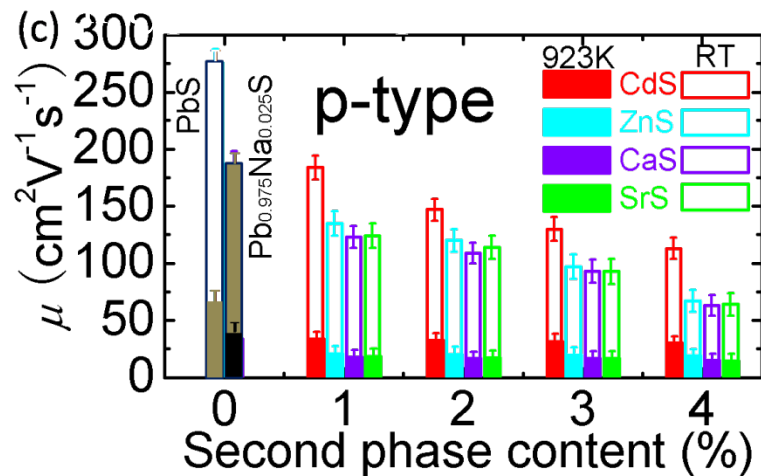
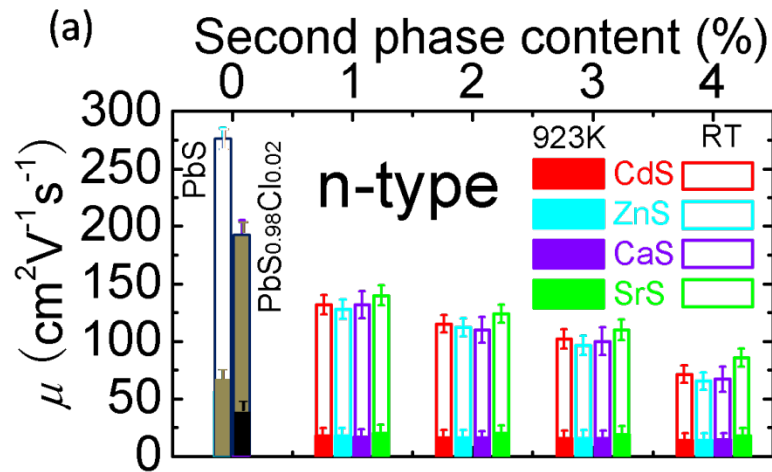
Calculated band gap energy levels of the metal sulfides, PbS, CdS, ZnS, CaS and SrS all in the NaCl structure. All values are in eV. (courtesy of Prof. C. Wolverton)

# TEM: nanostructured PbS

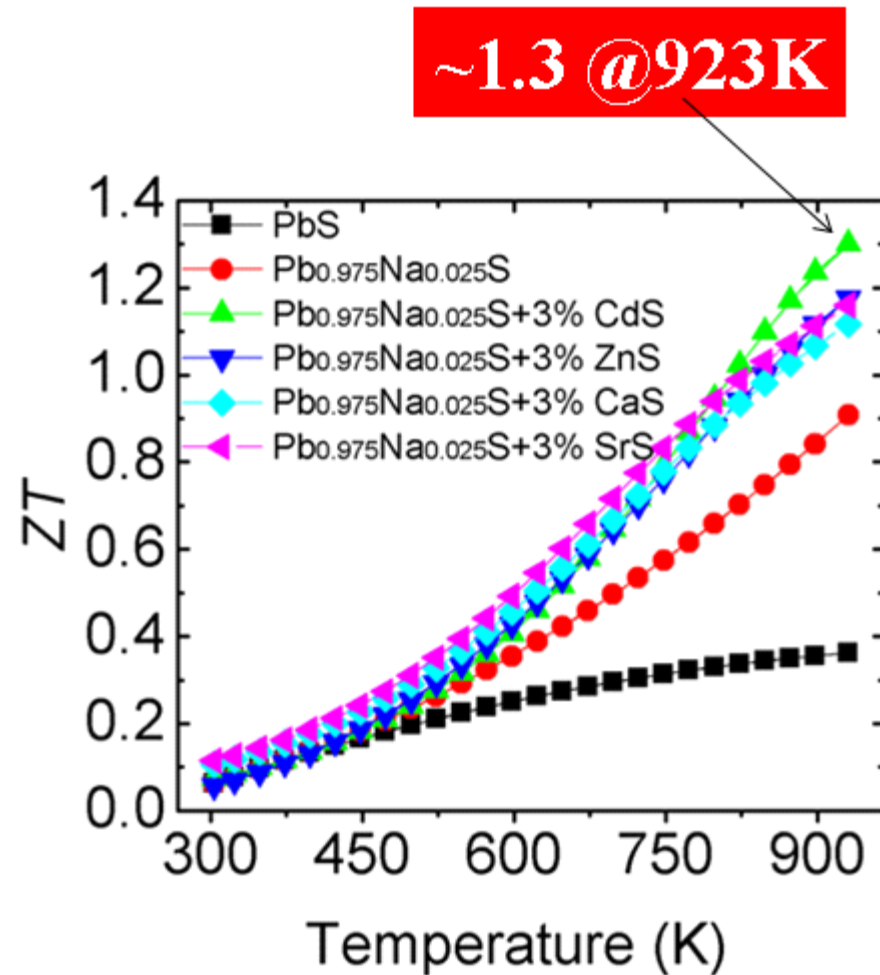
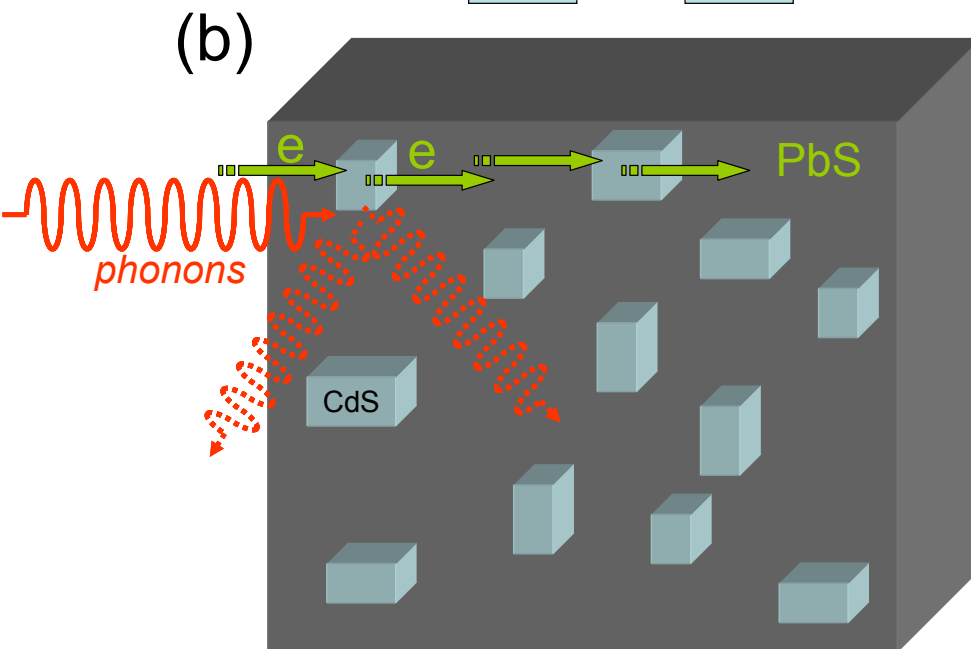
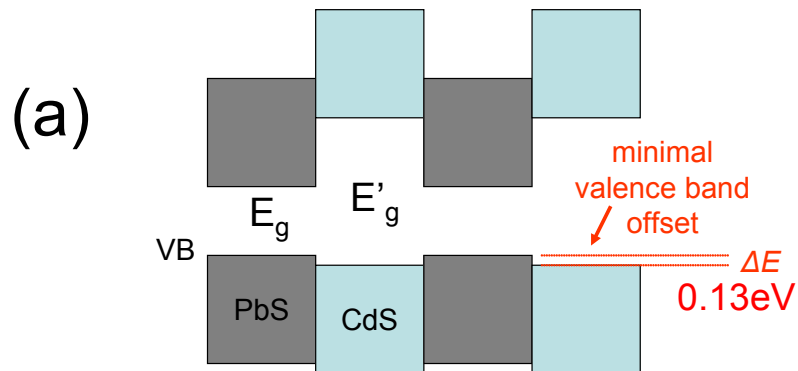




# P-type PbS: $\kappa_{\text{lat}}$ , $\mu_n$ and $\mu_p$



# ZT for PbS system



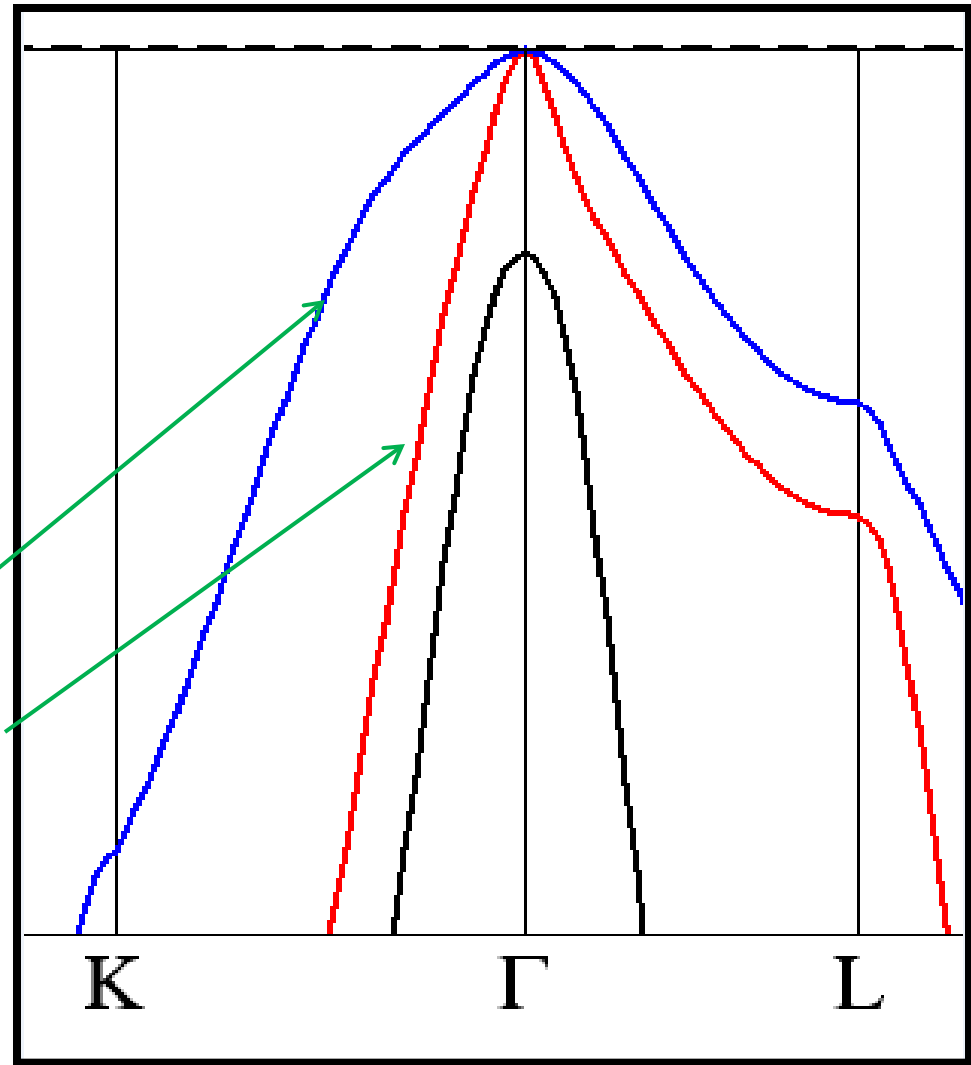
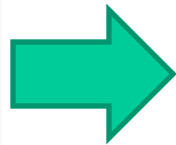
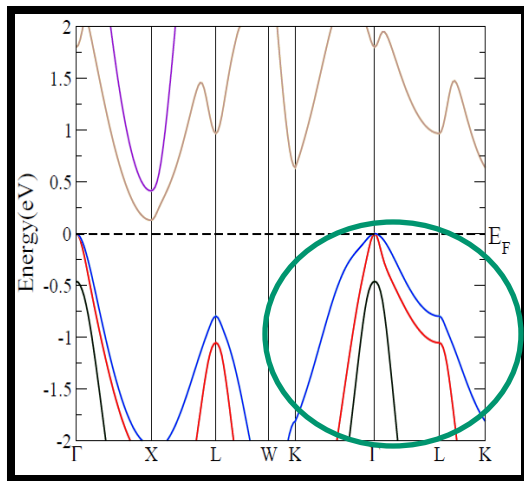


## Approach 2: Resonant levels in $\text{Mg}_2\text{Sn}_{1-x}\text{Si}_x$ (OSU)

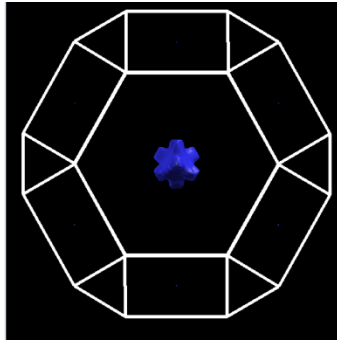
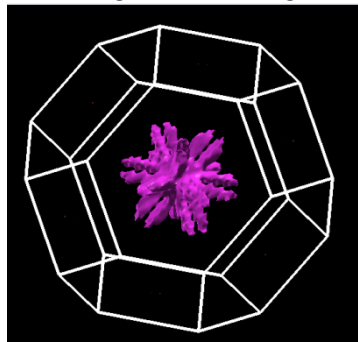
- Cheap , Environmentally friendly, & Abundantly available.
- N-type  
High ZT reported in  $\text{Mg}_2\text{Sn}_{1-x}\text{Si}_x$  (ZT >1)
  - Zaitsev et al. *Physical Review B* 74, 045207 (2006)
  - Q. Zhang et al. *Appl. Phys. Lett.* 93, 102109 (2008).
- P-type  
Few studies for P-type  $\text{Mg}_2\text{Sn}_{1-x}\text{Si}_x$  materials have been reported.
- Candidate dopants identified by band structure calculations (J. Tobola): Ag



# Calculated Masses & Fermi surface: favorable



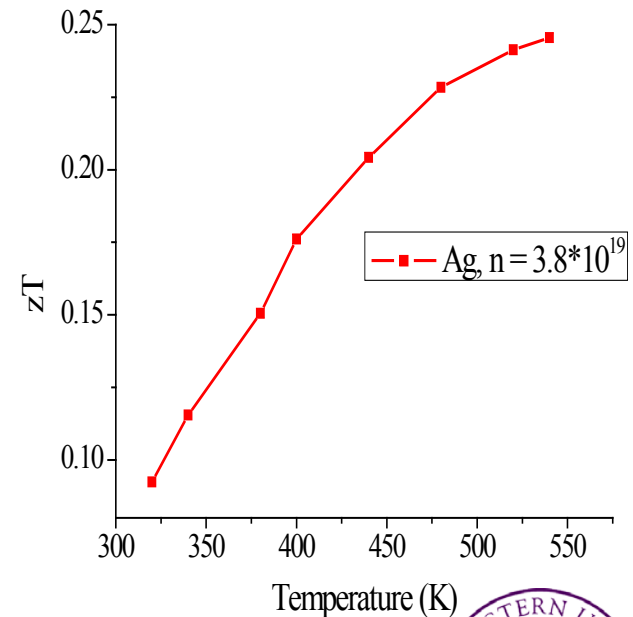
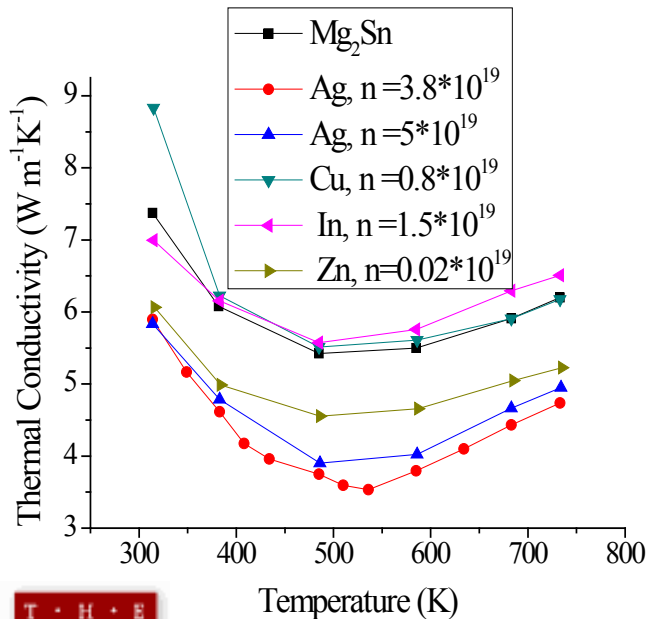
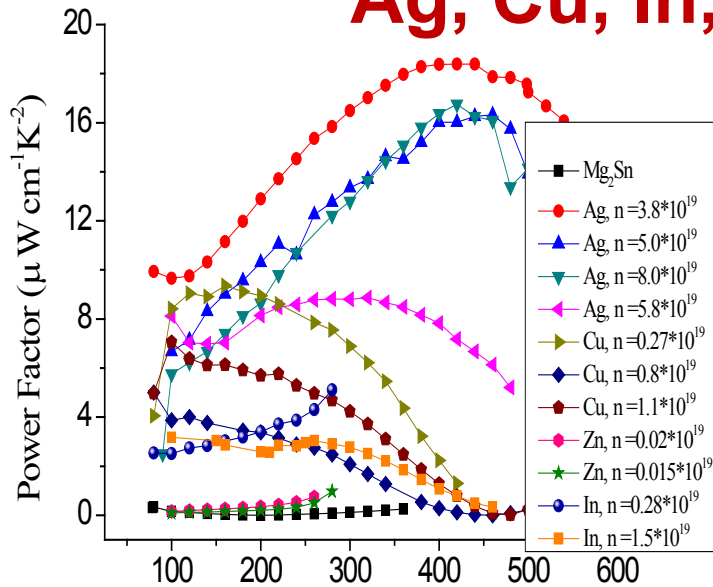
$0.7m_0 - 1m_0$  for heavy band,  
 $0.15m_0 - 0.2m_0$  for intermediate



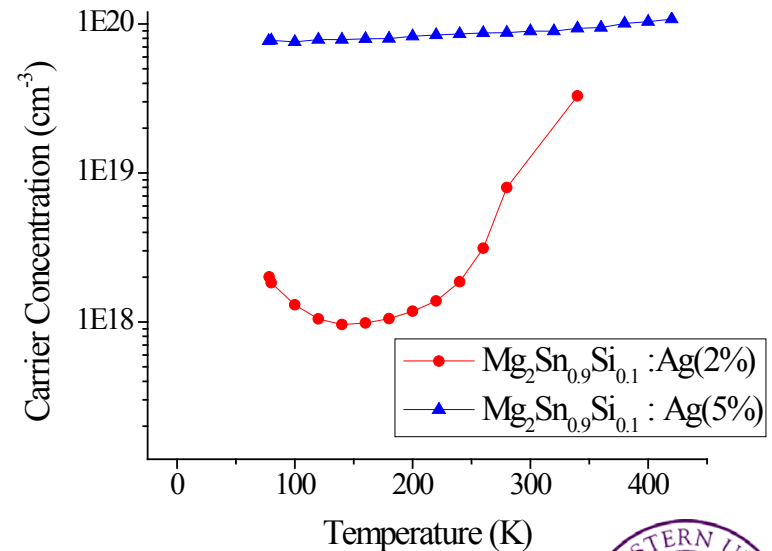
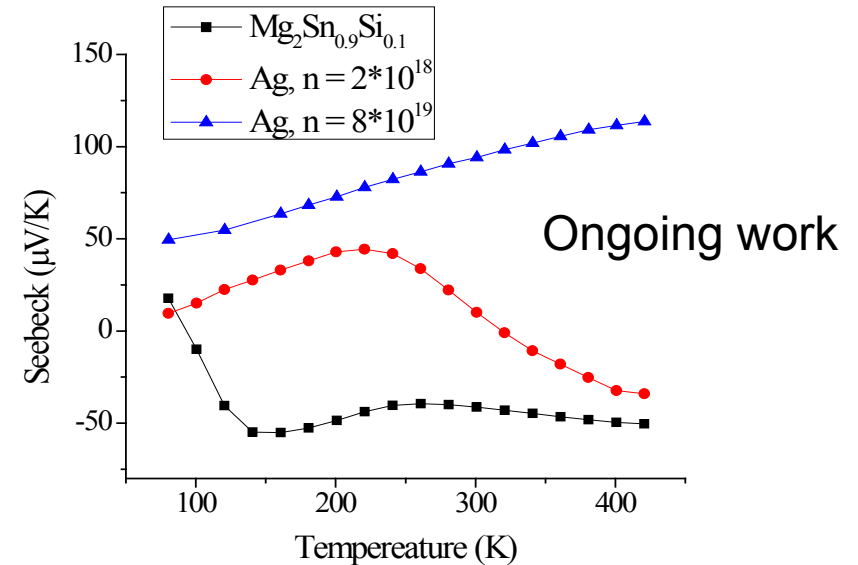
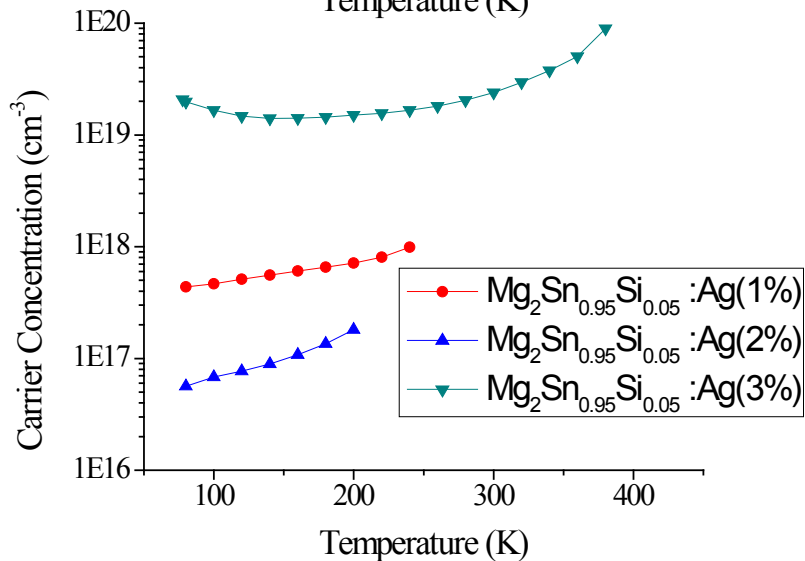
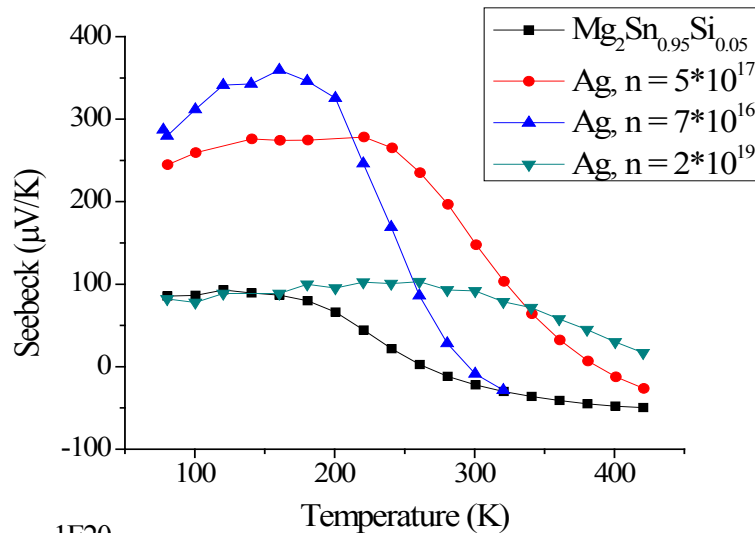
# Ag, Cu, In, Zn Doped Binary $\text{Mg}_2\text{Sn}$

Binary  $\text{Mg}_2\text{Sn}$  has

1. too high a thermal conductivity
2. too low a band gap  $\Rightarrow$  minority carriers appear at 400 K and decrease thermopower



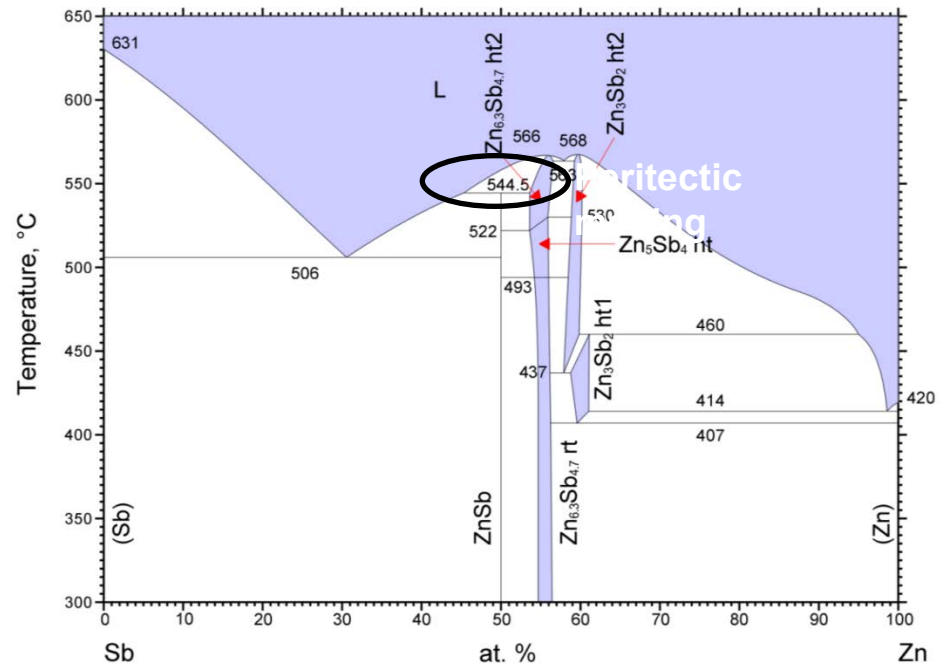
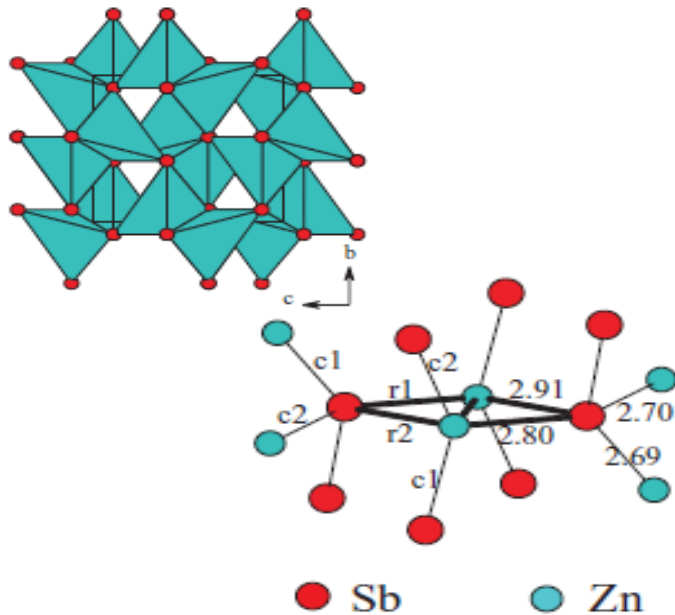
# Mg<sub>2</sub>Sn<sub>1-x</sub>Si<sub>x</sub> X = 0.1, 0.05, doped with Ag



# Approach 3: ZnSb (ZTPlus, OSU)

Cheap , Environmentally friendly, & Abundantly available.

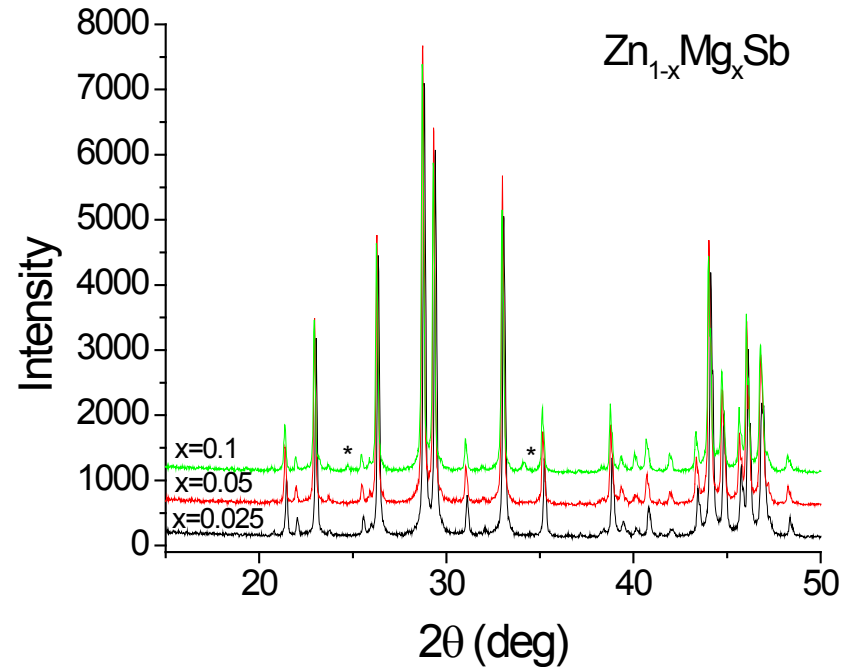
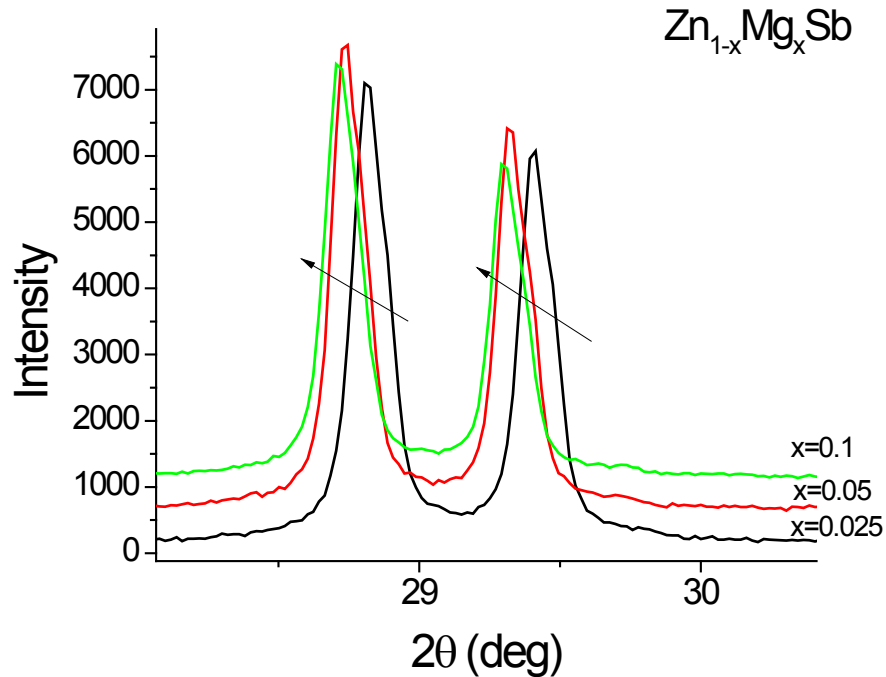
The peritectic melting of the phase generates impurities and degrades properties.



Usually extremely long post annealing times are required

SPS allows rapid production of 99% clean ZnSb specimens (XRD).

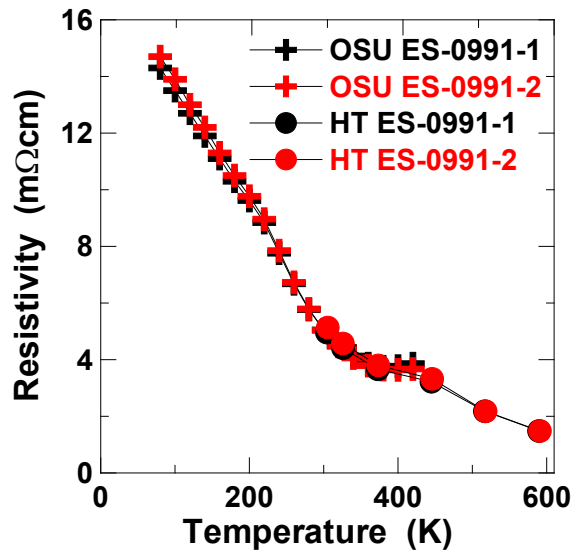
# $\text{Zn}_{1-x}\text{Mg}_x\text{Sb}$ alloys (ZTPlus)



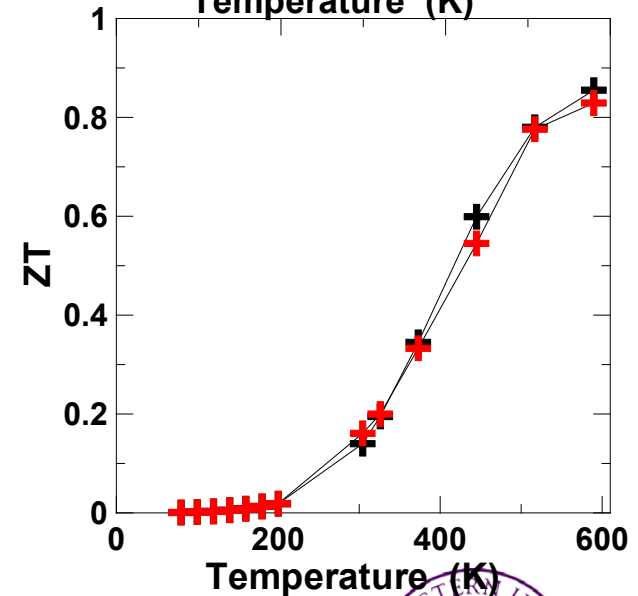
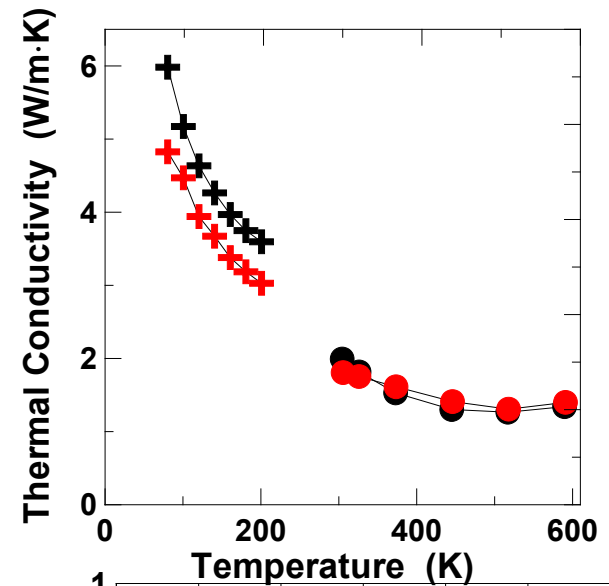
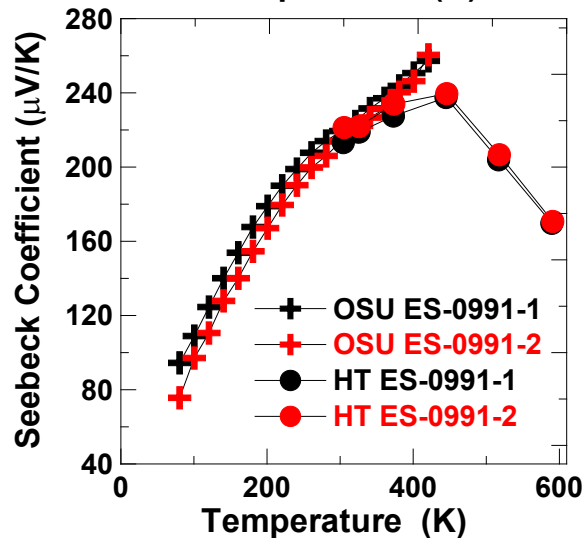
Can be alloyed with Mg (transport properties not yet studied)



# Transport properties of representative ZnSb sample

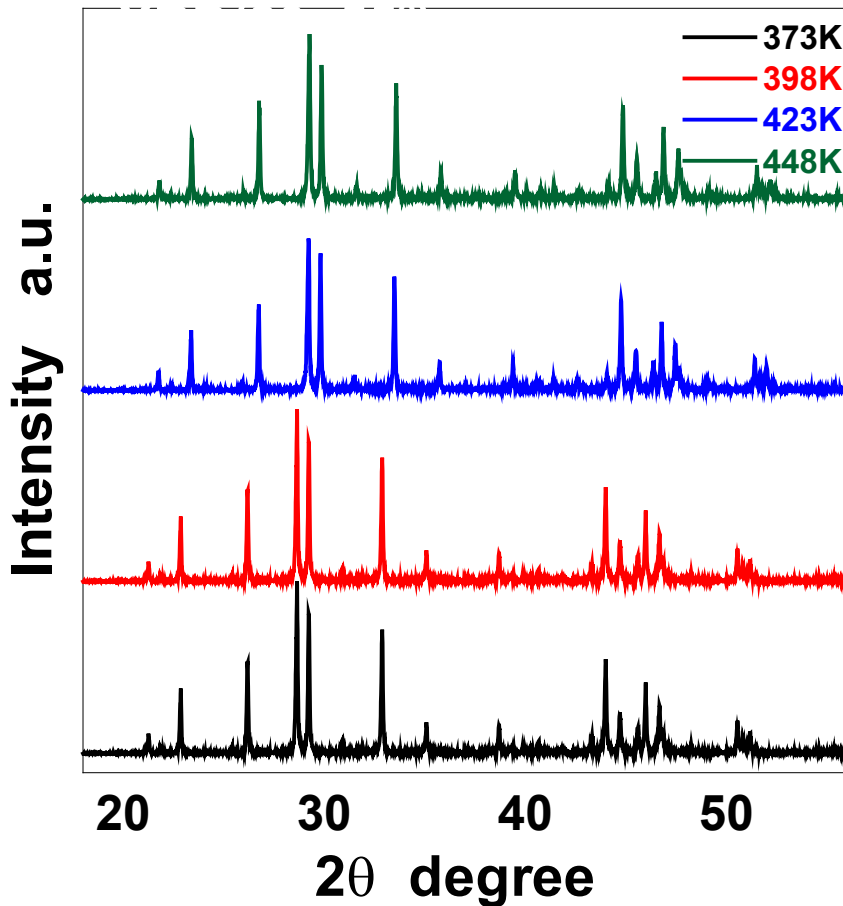


- Data obtained both at ZTPlus and at OSU
- Glitch at 423 K
- Excellent ZT

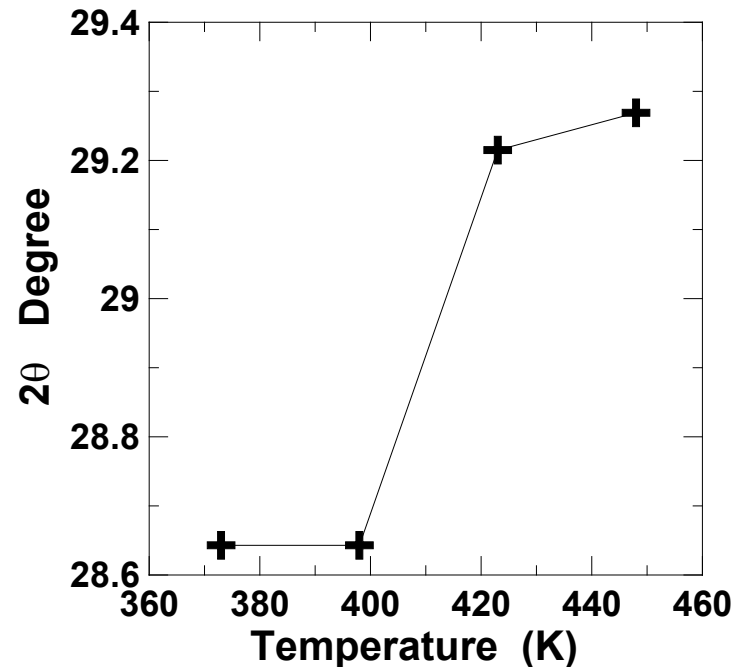


# High Temperature XRD on ZnSb

High Temperature XRD



Highest Peak Position vs T



- Peaks position change with temperature (thermal expansion)
- Abnormal jump between 398 and 423K (more measurements needed)

# Objective 3. Interfaces (Virginia Tech)

## Compliant, high electrical and thermal conductance

New compliant thermoelectric device interconnects using nanosilver

Problem addressed: interdiffusion between chalcogen atoms in thermoelectric material and silver in contacts

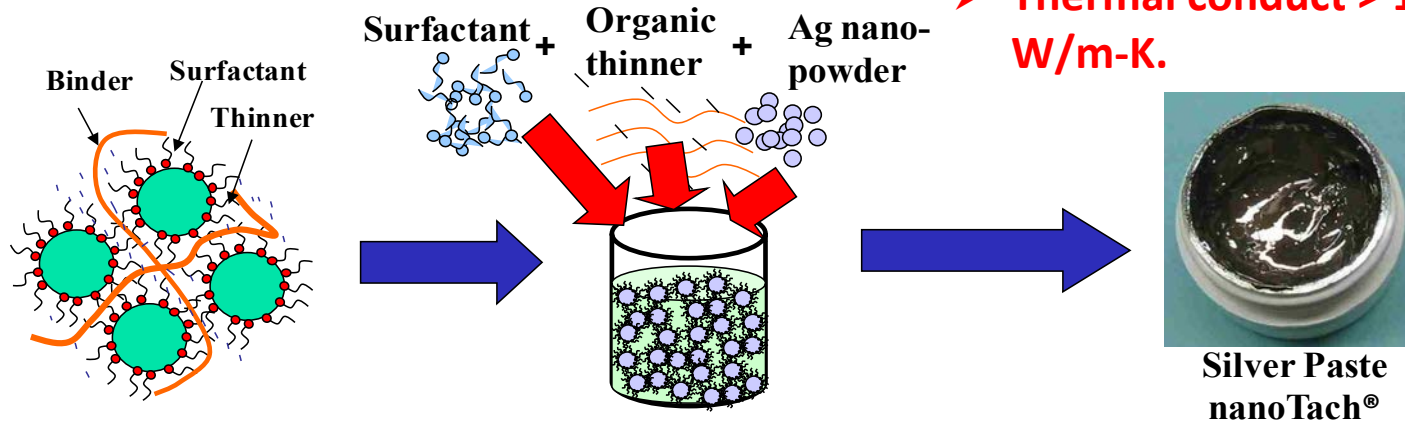
Achievement this year: diffusion barrier for thermoelectric materials



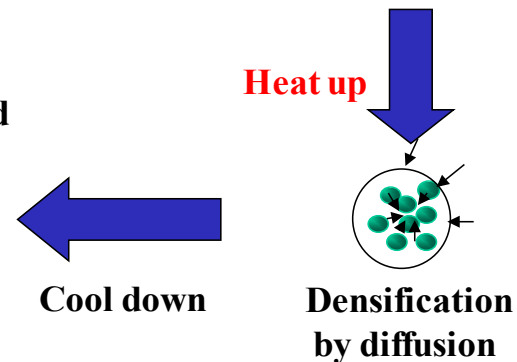
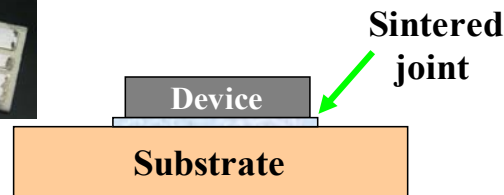
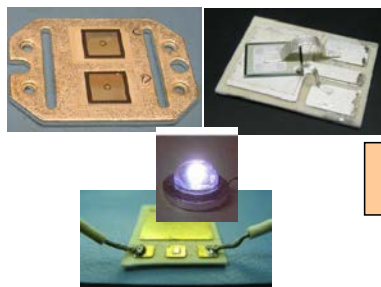
# Approach: Nanosilver interconnect packaging material

Pb-free, high-T die-attach solution:

- Joint formed below 280°C;
- Melting at 960°C;
- Thermal conduct > 150 W/m-K.

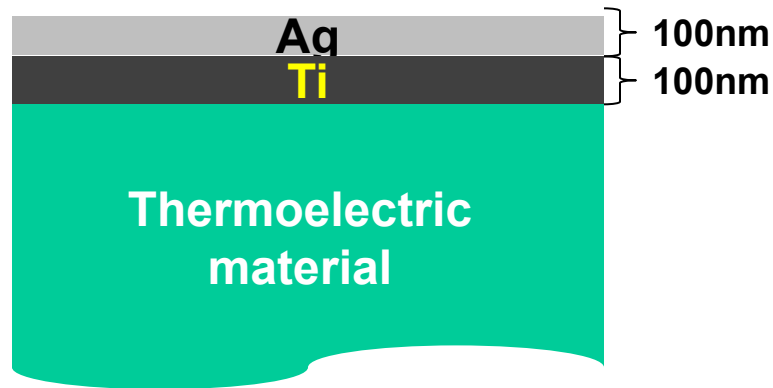


Assembled TE device

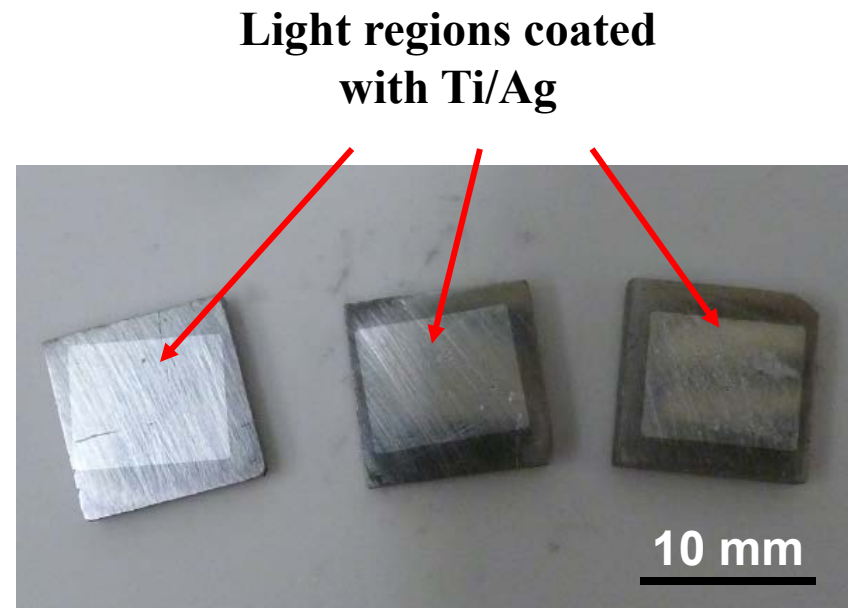


# Diffusion barrier: vapor deposition of Ti/Ag interface layer on thermoelectric substrate

Objective: to metallize  $\text{Bi}_2\text{Te}_3$ -based thermoelectric material with diffusion barrier layer for bonding by nanosilver paste.



**Schematic of Ti/Ag layer deposited on TE material**



**TE materials with Ti/Ag deposited as the coating layer**

# Evaluation of film adhesion by scratch-test



**As-coated sample**



**Scratched by a diamond scribe, then peeled by adhesive tape**



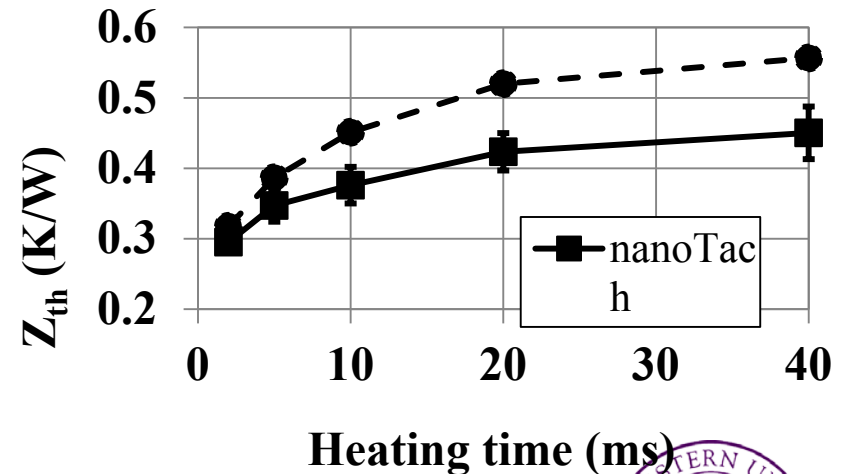
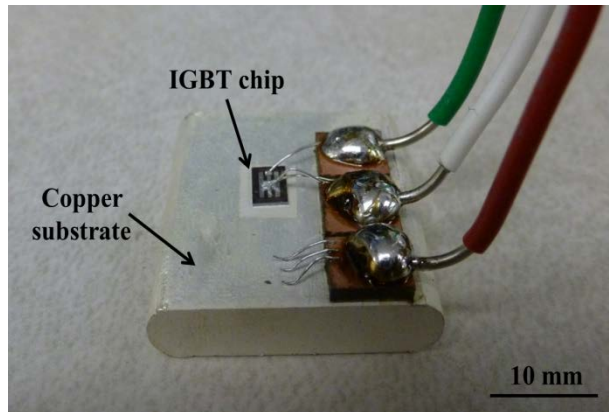
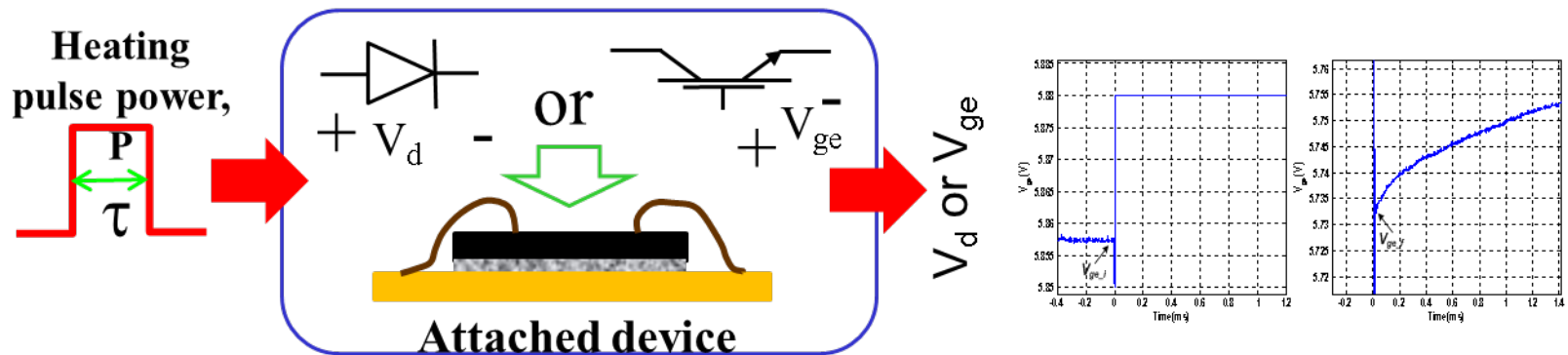
**Enlarged view of the tested region**

- ✓ The fact that the coating did not come off completely with the tape suggests that the adhesion is reasonably strong.
- ✓ Work is underway to quantify the adhesion strength.

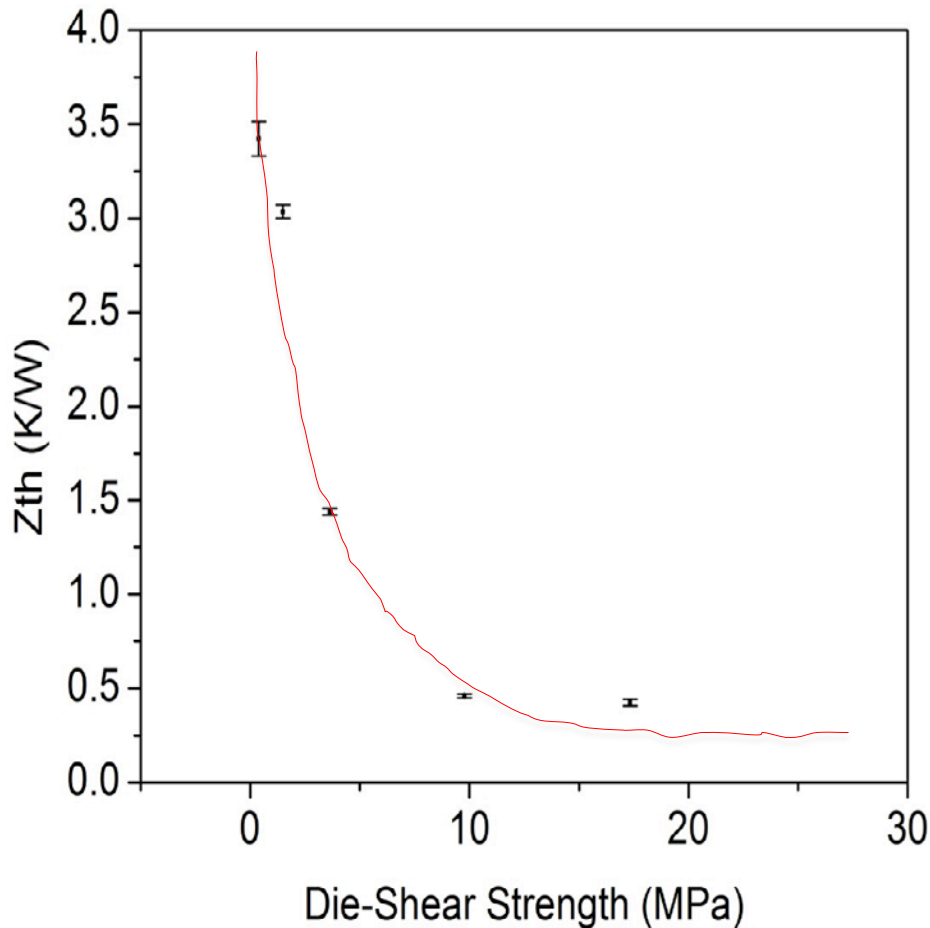


# Objective 4. Metrology: thermal contact resistance measurements

Objective: to determine the thermal property of nanosilver-bonded interface from bonding strength measurement.



# Thermal impedance vs. die-shear strength



Observations:

- ❑ Thermal impedance decreases drastically with increasing die-shearing strength;
- ❑ A die-shear strength of at least 10 MPa is necessary for low thermal impedance.

## Objective 5. Durability

### Ensure that this project incorporates automotive durability standards.

1. Durability is built into every step of the design
2. Thermal stability of PbS' ZT (backup slide only)
3. Extensive durability testing at Gentherm and ZTPlus

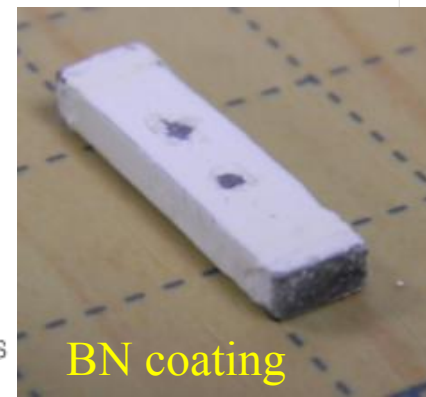
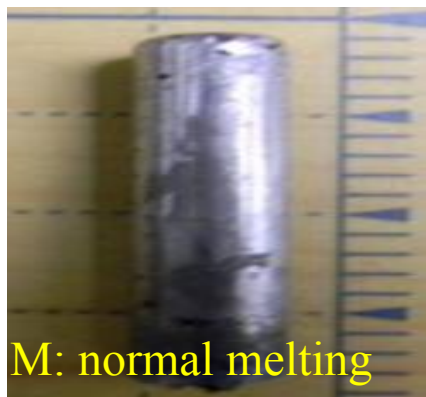
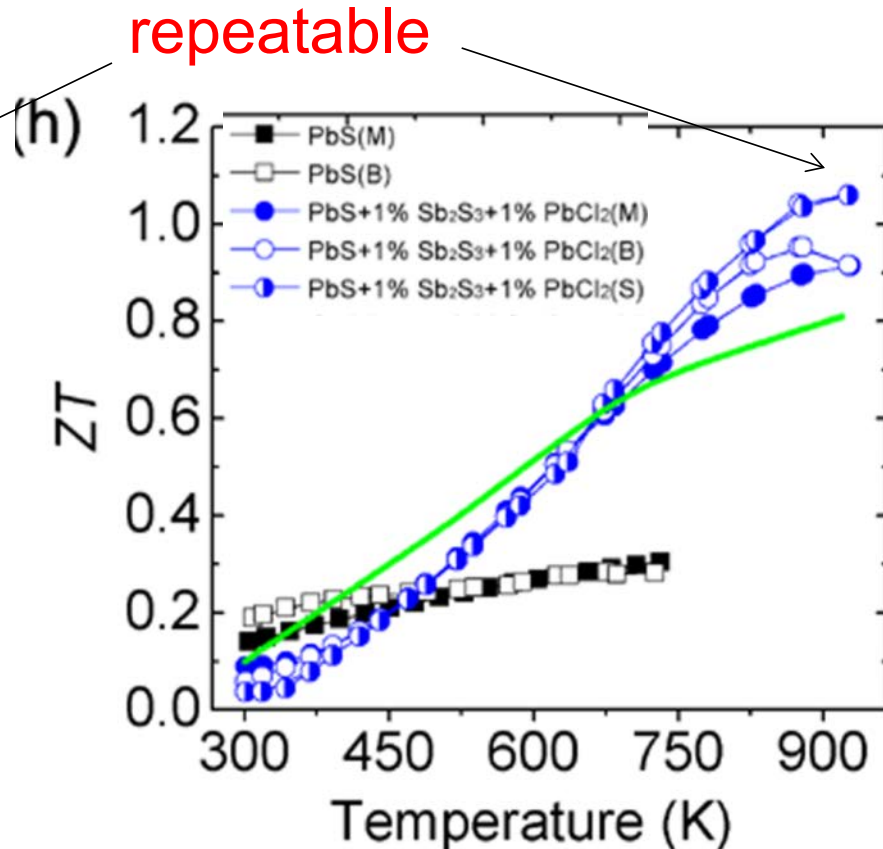
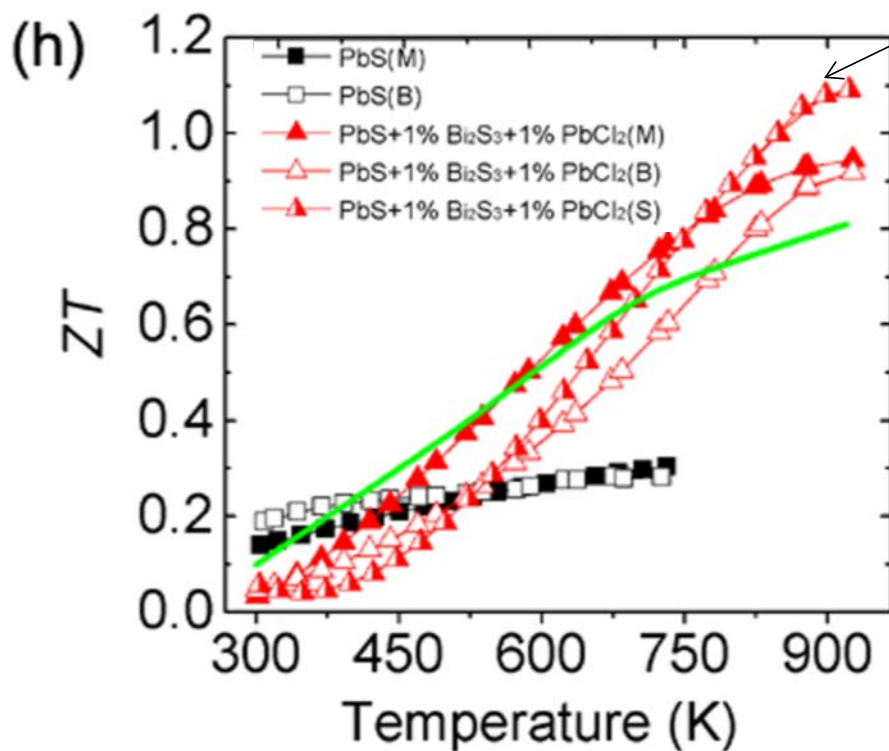
Gentherm and ZTPlus, have state-of-the-art durability testing facilities used in the development of automotive products.

Achievement this year:

**thermal cycling resistance of newly developed materials**  
**reproducibility of newly developed materials**

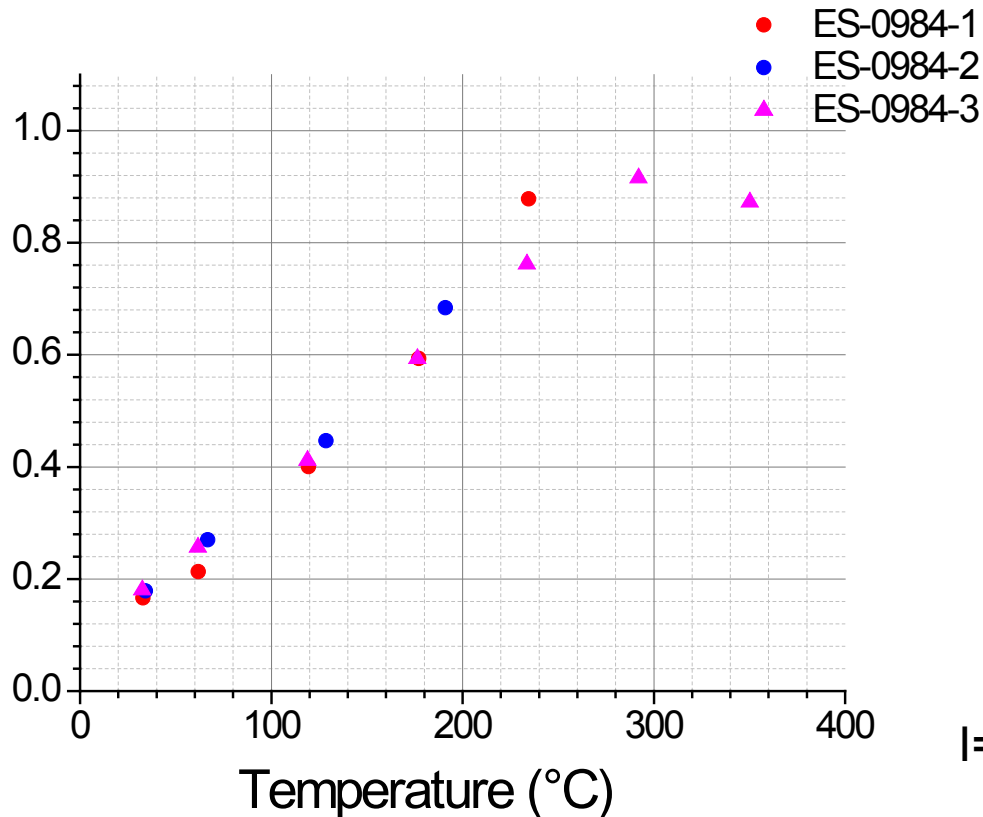


# Repeatability of n-type PbS, $ZT=1.1$



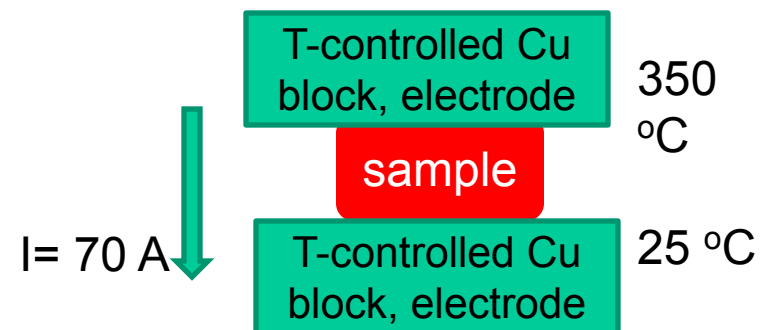
# ZnSb (ZTPlus) figure of merit, thermal stability

## THERMAL STABILITY TESTS



50 cycles between 30 to 370 °C: No degradation of properties. Improvement of the power factor.

In-gradient testing 48 hours: sample chemically stable repeated properties



# SUMMARY: FIVE objectives

## 1. New Materials

- **PbS record ZT achieved**; literally dirt-cheap
- $\text{Mg}_2(\text{Si}, \text{Sn})$ : Doping studies of p-type material
- ZnSb: excellent ZT up to 0.85, repeatable

## 2. Gentherm thermal design used in prototypes (not developed under this program)

## 3. New Interface technologies: flexible Ag nanopaste

- Developed diffusion barrier layer

## 4. Metrology:

- 1. Thermal contact resistance measurements, the role of die-attach bond strength

## 5. Reliability: inherent in design

- 1. Data on reproducibility of PbS
- 2. Data on cyclability of ZnSb

Collaboration is inherent, flow of materials from partner to partner.





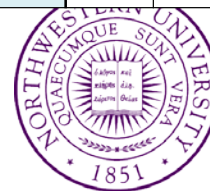
# Technical back-up slides



# Milestones (bold = achieved, ← = pulled forward)

**Summary: record ZT's achieved after year 1 => expand to cheaper alternative PbS**

Project Phase			Years 1 – 3		
Task	Description	Time Period in years	1	2	3
<b>1</b>	<b>Optimize thermoelectric properties of PbSe</b>				
1.1	Determine conditions for thermodynamic synthesis		X		
1.2	Develop bulk nanostructuring material by liquid encapsulation for Sb-PbSe, Bi-PbSe, Ga-PbSe, In-PbSe, As-PbSe		X	X	X
1.2.1	Chemical characterization (XRD/SEM/EDX)		X	X	X
1.2.2	Thermoelectric characterization: measuring, analyzing		X	X	
1.3	Introduce resonant impurities (In, Al, Ga, Tl)		X	X	X
1.3.1	Chemical characterization (XRD/SEM/EDX)		X		
1.3.2	Thermoelectric characterization: measuring, analyzing		←	X	X
1.4	Introduce 3d,4d or 5d elements and tune		←	X	X
1.4.1	Chemical characterization (XRD/SEM/EDX)		←	X	X
1.4.2	Thermoelectric characterization: measuring, analyzing		←	X	X



<b>2</b>	<b>Optimize thermoelectric properties of <math>\text{Mg}_2\text{X}</math> (Si,Sn,Pb)</b>			
2.1	Determine conditions for thermodynamic synthesis	<b>X</b>		
2.2	Develop bulk nanostructuring material by liquid encapsulation for $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x/\text{Y}$ , $\text{Mg}_2\text{Si}_{1-x}\text{Pb}_x/\text{Y}$ , $\text{Mg}_2\text{Sn}_{1-x}\text{Pb}_x/\text{Y}$ with $\text{Y} = \text{W, Mo, Ta, Hf, Nb}$	<b>X</b>	X	X
2.2.1	Chemical characterization (XRD/SEM/EDX)	←	X	X
2.2.2	Thermoelectric characterization: measuring, analyzing	←	X	X
2.3	Extend investigation with $\text{Y} = \text{stannides}$ ( $\text{Hf}_5\text{Sn}_3$ , $\text{HfSn}$ , $\text{La}_3\text{Sn}_5$ , $\text{LaSn}_3$ , $\text{CoSn}$ , $\text{FeSn}$ )			X
2.3.1	Chemical characterization (XRD/SEM/EDX)			X
2.3.2	Thermoelectric characterization: measuring, analyzing			
2.4	Extend investigation with $\text{Y} = \text{silicides}$ ( $\text{Co}_2\text{Si}$ , $\text{CoSi}$ , $\text{CoSi}_2$ , $\text{NiSi}_2$ ( $\text{CaF}_2$ type), $\text{FeSi}$ , $\text{LiAlSi}$ , $\text{ZrSi}_2$ , $\text{Zr}_2\text{Si}$ , $\text{Zr}_3\text{Si}$ , $\text{Hf}_2\text{Si}$ , $\text{Hf}_3\text{Si}_2$ , $\text{WSi}_2$ , $\text{W}_5\text{Si}_3$ , $\text{RuSi}$ )			X
2.4.1	Chemical characterization (XRD/SEM/EDX)			X
2.4.2	Thermoelectric characterization: measuring, analyzing			X
2.5	Introduce resonant level in $\text{Mg}_2\text{Pb}_{1-x}\text{X}_x$ $\text{X} = \text{Sb, Bi}$ for n-types	<b>X</b>	X	
2.5.1	Chemical characterization (XRD/SEM/EDX)		X	
2.5.2	Thermoelectric characterization: measuring, analyzing		X	X
2.6	Introduce resonant level in $\text{Mg}_2\text{Pb}_{1-x}\text{X}_x$ $\text{X} = \text{Ga, In}$ for p-type or by substituting Mg by Na, Ag,		X	X
2.6.1	Chemical characterization (XRD/SEM/EDX)		X	X
2.6.2	Thermoelectric characterization: measuring, analyzing		X	X

# Milestones (bold = achieved, ← = pulled forward)

<b>3</b>	<b>Metallization of TE materials</b>			
3.1	For PbSe-based material (SPS)	<b>X</b>		
3.1.1	Develop blend of Fe/Sn or Pb chalcogenides	<b>X</b>		
3.1.2	Chemical characterization of intermetallics (SEM/EDX)	<b>X</b>		
3.1.3	Co-pressed the blend with PbSe by SPS	X	X	
3.1.4	Chemical characterization of intermetallics (SEM/EDX)	X	X	
3.1.5	Optimize densification properties	X	X	
3.1.6	Measurement of the contact resistance	X	X	X
3.1.7	Durability test (thermal cycling and chock resistance)		X	X
3.1.8	Explore other barriers of diffusion co-pressed by SPS	←	X	X
3.2	For PbSe-based material (PVD)	X		
3.2.1	Identify potential element (e.g. nitride or carbide)		X	
3.2.2	Development of the sputtering process		X	
3.2.3	Chemical characterization (SEM/EDX)		X	X
3.2.4	Measurement of the contact resistance		X	X
3.2.5	Durability test (thermal cycling and chock resistance)		X	X

# Milestones

<b>3</b>	<b>Metallization of TE materials</b>			
3.3	Develop a process for $\text{Mg}_2\text{X}$ (SPS)		X	X
3.3.1	Identify potential blend		X	X
3.3.2	Co-pressed the blend with $\text{Mg}_2\text{X}$ by SPS		X	X
3.3.3	Chemical characterization of intermetallics (SEM/EDX)		X	X
3.3.4	Optimize densification properties		X	X
3.3.5	Measurement of the contact resistance			X
3.3.6	Durability test (thermal cycling and chock resistance)		X	X
3.4	Develop a process for $\text{Mg}_2\text{X}$ (PVD)		X	
3.4.1	Identify potential element (e.g. nitride or carbide)		X	X
3.4.2	Development of the sputtering process		X	
3.4.3	Chemical characterization (SEM/EDX)		X	
3.4.4	Measurement of the contact resistance			X
3.4.5	Durability test (thermal cycling and chock resistance)			X



# Milestones (bold = achieved, ← = pulled forward)

<b>4</b>	<b>Device interconnection (bonding element to heat spreader)</b>			
4.1	Chemical investigation of Ag diffusion in metallization (SEM/XPS)	<b>X</b>		
4.1.1	Influence of the amount of Ag	<b>X</b>		
4.1.2	Influence of coating gold on Ag joint	X	X	
4.1.3	Measurement of the contact resistance	X	X	
4.2	Study of other metals (M)	←		X
4.2.1	Chemical investigation of M diffusion in metallization (SEM/XPS)	←		X
4.2.2	Influence of the amount of M	←		X
4.2.3	Measurement of the contact resistance	X	X	X

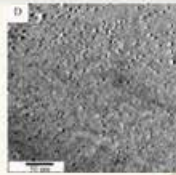


# Milestones (bold = achieved, ← = pulled forward)

<b>5</b>	<b>Integration of material and interfaces into patented module</b>			
5.1	Chemical characterization (XRD/SEM/EDX)		X	
5.2	Measurement of the contact resistance		X	X
5.3	Thermoelectric characterization: measuring, analyzing			x
5.4	Durability test	<b>x</b>	x	x
<b>6</b>	<b>Develop new module/heat exchanger design</b>			
6.1	Chemical characterization (XRD/SEM/EDX)		X	
6.2	Thermoelectric characterization: measuring, analyzing		X	X
6.3	Measurement of the contact resistance		X	X
6.4	Durability test		X	X

## 1. Materials

NU – OSU  
PbSe –based or  
 $Mg_2X$  ( $X=Ge, Si, Sn, Pb$ )

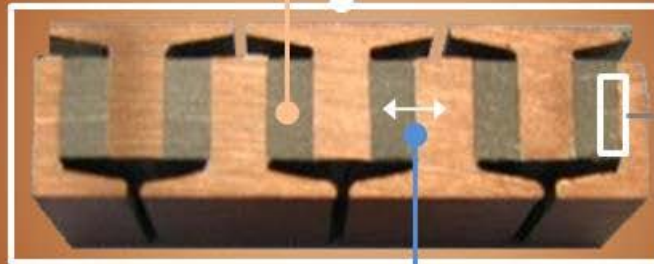


## 2. Thermal Management

BSST  
Innovative  
Design and Architecture

## 5. Durability

BSST – OSU – NU  
VT – ZTPlus  
Mechanical and  
Thermal shock  
resistance



## 4. Metrology

BSST – OSU – NU  
VT – ZTPlus  
(ITE)

Chemical and Physical  
characterization

## 3. Interfaces

VT – ZTPlus  
New flexible  
Ag Nanopaste and  
metallization

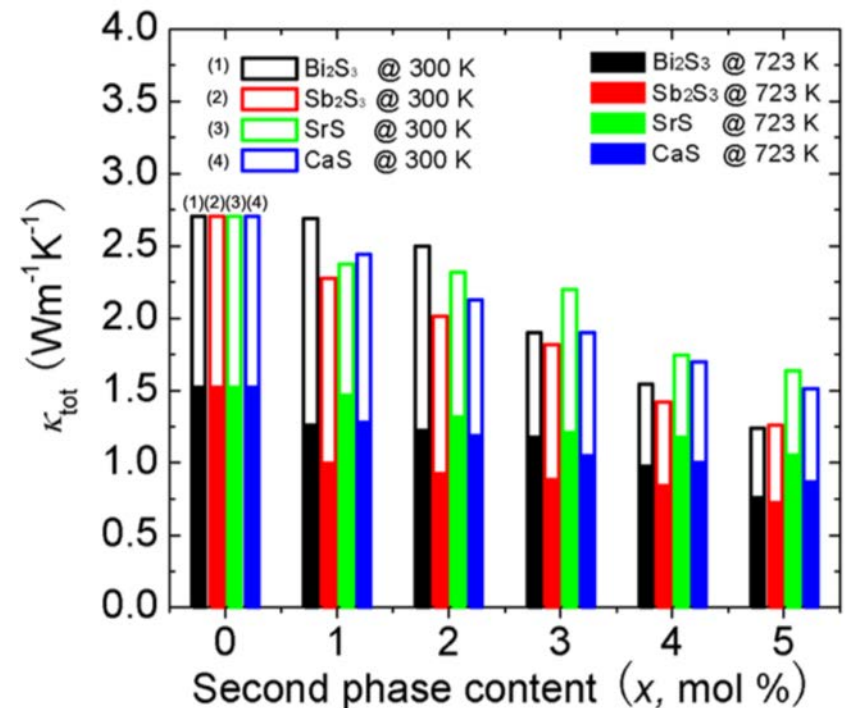
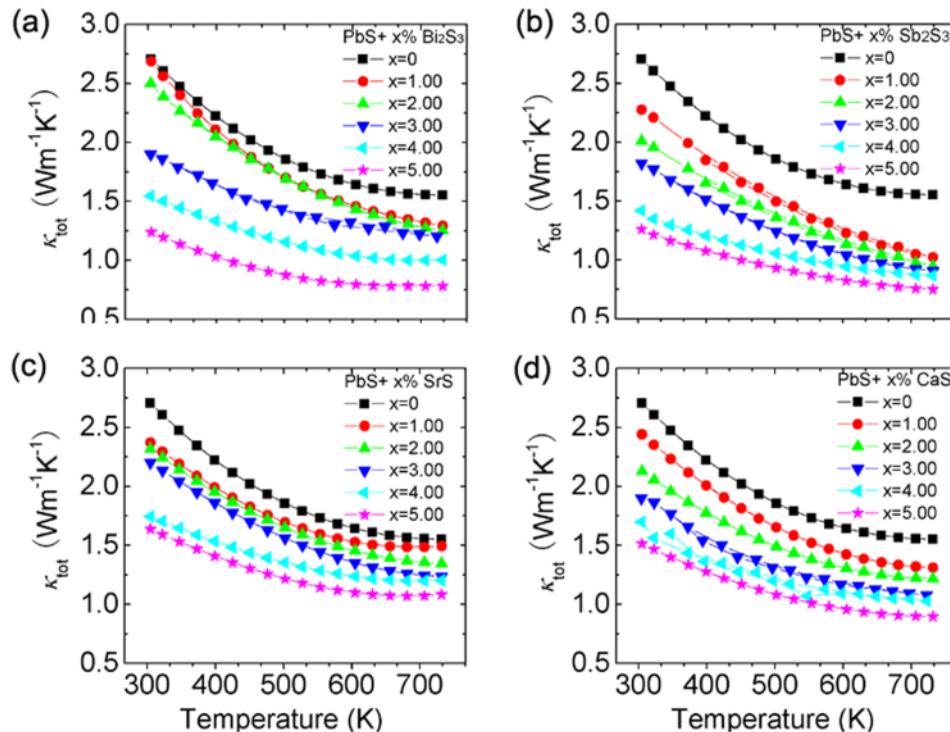


# n-type PbS with second phases

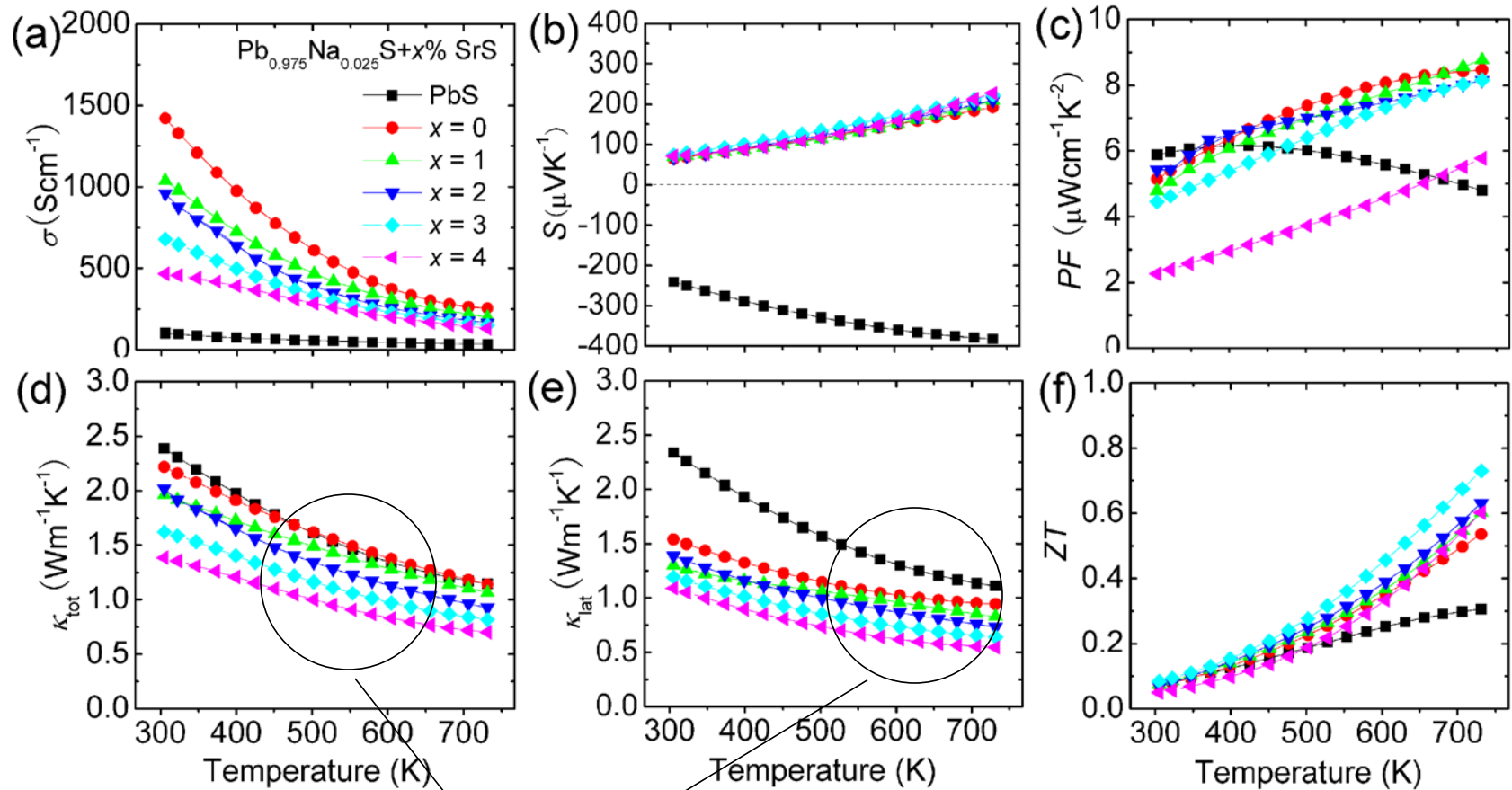
PbS: the cheapest thermoelectric

Band alignment engineering between nanostructures and matrix is a key path forward to increasing ZT

High performance in nanostructured p-type PbS ( $ZT \sim 1.2-1.3$  at 900 K): This is a breakthrough in the performance of PbS

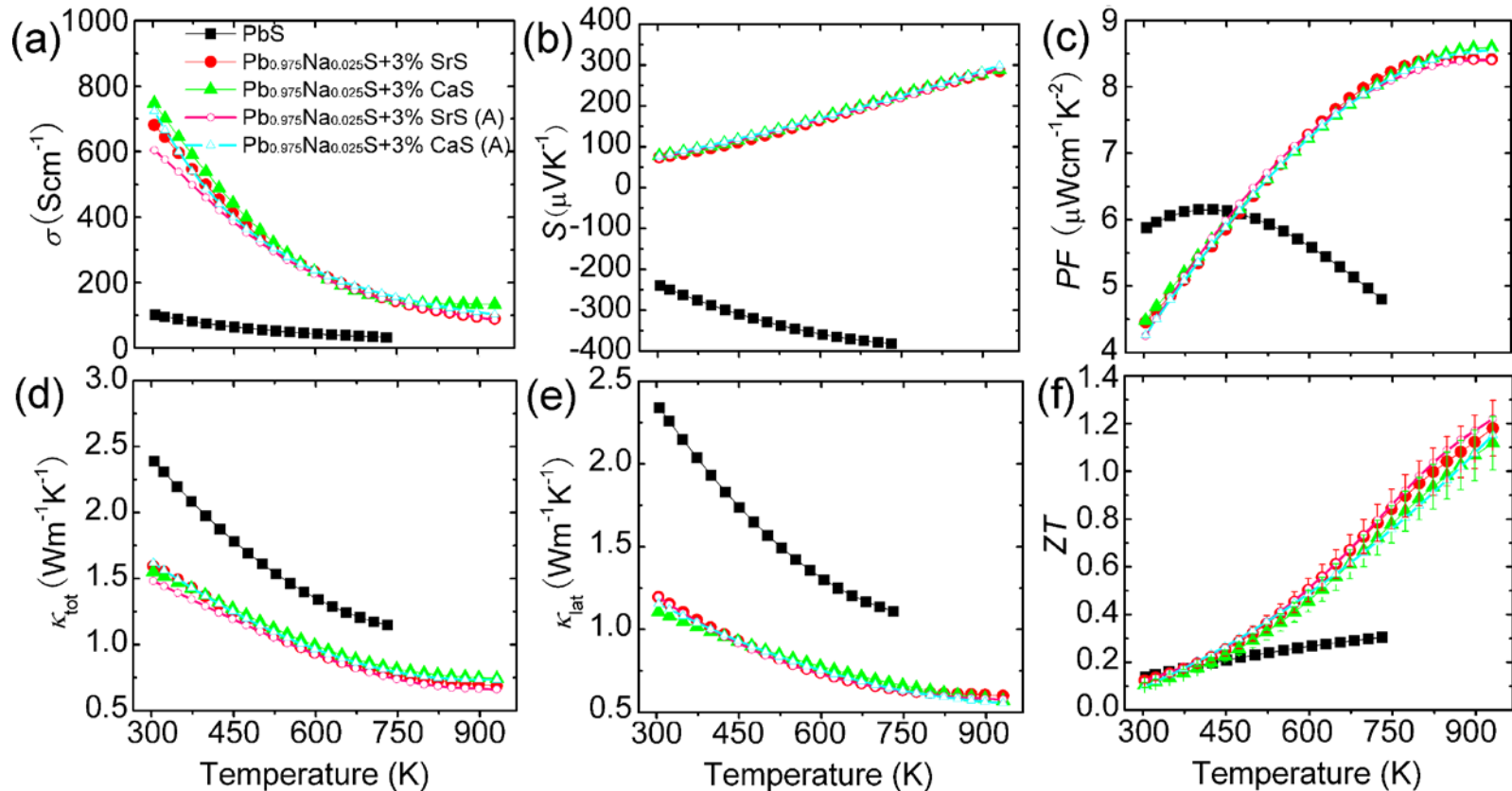


# P-type $\text{Pb}_{0.975}\text{Na}_{0.025}\text{S-x}\%\text{SrS}$



Both total and lattice  $\kappa$  were reduced by SrS inclusions

# Pb<sub>0.975</sub>Na<sub>0.025</sub>S-3%CaS/SrS & thermal stability



Pb<sub>0.975</sub>Na<sub>0.025</sub>S+3%SrS shows  $ZT$  about 1.2 at 923K,

Pb<sub>0.975</sub>Na<sub>0.025</sub>S+3%CaS shows  $ZT$  about 1.1 at 923K,

both samples show excellent thermal stabilities after annealing treatments.



# Concept adapted from PbTe work

